Oxygen 1s XAS of H_2O in the solvation shell of ions

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INTRODUCTION

By using the high intensity of the underlator beamline 8.0 and the Soft X-ray Endstation for Environmental Research (SXEER), we now can probe the molecular orbital structure of liquid water. Near-Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy at the Oxygen K-absorption edge will give some information of the Oxygen p-character and hence the local geometric arrangement around the probed oxygen atom. A NEXAFS spectrum of pure liquid water, see figure 1, has a pronounced pre-edge peak below the main absorption edge. This pre-edge peak originates from specific configurations of water, for which the hydrogen bonding is unsaturated and strongly asymmetric [1].

OXYGEN 1s XAS OF WATER WITH DISSOLVED SALTS

Water in its natural environment has major contributions of various dissolved compounds such as salts, minerals, organic molecules, pollution's etc. The water molecules will interact with all these soluble (and insoluble) elements. If we for example dissolve Potassium Chloride (KCl) into water, the water molecules will form a so-called solvation shell around each Potassium- and Chloride ion. These water molecules will be oriented in a special way and give the Oxygen atom a surrounding different from an Oxygen atom in the bulk water. In figure 2 there is a NEXAFS spectrum at the Oxygen edge of water with dissolved KCl. If we have a look at the peak in the pre-edge area, we can see a shoulder that probably originates from the water molecules in the solvation shells. The shoulder is more pronounced at higher concentration.

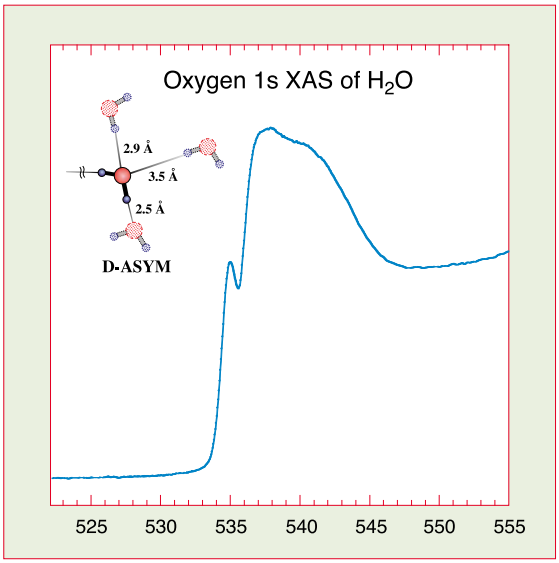

Figure 1. Oxygen 1s XAS of pure water. The pre-edge peak originates from the unsaturated and strongly asymmetric water molecules with a broken Hydrogen bond.

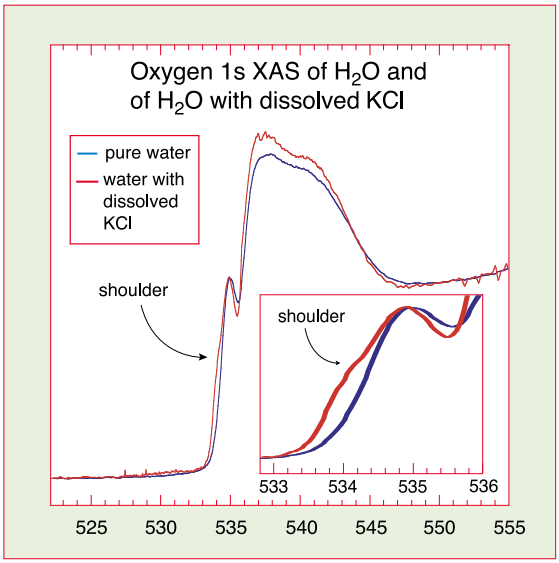

Figure 2. Oxygen 1s XAS of water with dissolved Potassium Chloride. The shoulder at the pre-edge peak originates from water molecules in the solvation shell of the dissolved ions.

OXYGEN 1s XAS OF WATER WITH TRANSITION METAL IONS

A transition metal ion will also interact with water. A NEXAFS spectrum of water with dissolved Ferric Chloride ($FeCl_3$) is shown in figure 3a. As expected this spectrum is similar to the pure water spectrum, but if we enlarge the area below the pre-edge peak, figure 3b, we can see some new features. There are two small peaks at 530.0 and 531.4 eV respectively, and a broad shoulder between the two peaks and the pre-edge peak at 535 eV. We interpret that these features originate from d-orbital interactions between the $FeCl_x$ ion and the water molecules. Preliminary calculations are supporting this idea, but further measurements and calculations are needed before a reliable interpretation is possible.

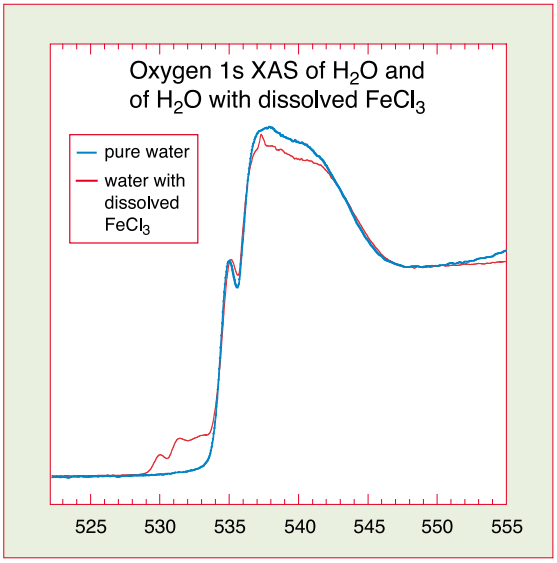

Figure 3a. Oxygen 1s XAS of water with dissolved Ferric Chloride ($FeCl_3$) compared with pure water. Before the pre-edge peak there are some structures in the water with dissolved $FeCl_3$ that not exist in the pure water.

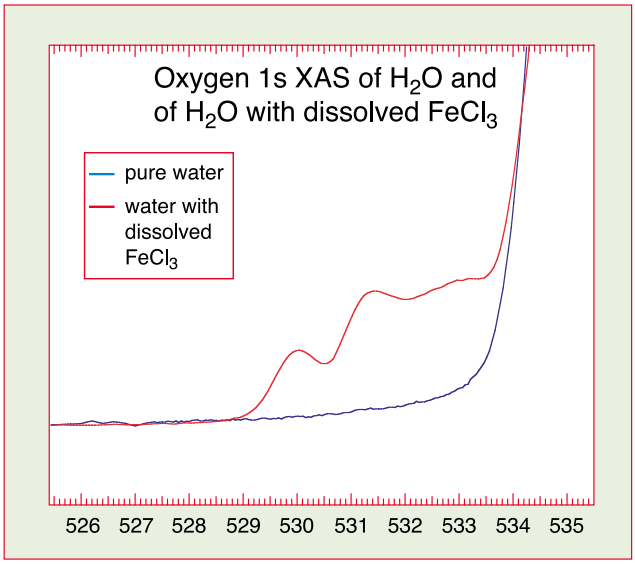

Figure 3b. The area below the pre-edge peak enlarged. There are two small peaks at 530.0 and 531.4 eV respectively, and a broad shoulder between the two peaks and the pre-edge peak at 535 eV.

When $FeCl_3$ is dissolved into the water, the solution contains different species of Fe-Cl complexes with solvation shells. The 1st solvation shell can hold up to six water molecules, (Fe^{3+} x 6 H_2O) [2]. But most likely there are $FeCl^{2+}$ and $FeCl_2^{+}$ in our sample, with 5 H_20 and 4 H_2O respectively in the 1st solvation shell. The 2nd solvation shell has 12 water molecules [2], and after that the water molecules will have a surrounding that are more like bulk water.

ACKNOWLEDGMENTS

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REFERENCES

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